COMPOSITE CATALYST FOR THE SELECTIVE OLIGOMERIZATION OF
LOWER ALKENES AND THE PRODUCTION OF HIGH OCTANE PRODUCTS

FIELD OF THE INVENTION

This invention relates to the oligomerization of lower
5   alkenes and mixtures of alkenes by catalytic distillation.
More specifically, the invention relates to a catalytic
composite as a catalyst and packing media in a catalytic
distillation column for the selective oligomerization of
lower alkenes. In addition, the invention also relates to
10   the hydrogenation of alkenes or of the products from the
selective oligomerization to produce high octane products.

BACKGROUND OF THE INVENTION

Catalytic distillation (CD) combines catalytic reaction and
separation in a single distillation unit. This idea was
15   first implemented early in the 1920s for the production of
esters (Backhaus, 1921) and has been applied to a number of
chemical processes based on homogeneous catalysts. The
advantages of combining reaction and separation were not
fully appreciated until 1980, when Smith patented a new
20   catalytic distillation technology using heterogeneous
catalysts (Smith, 1980).

Conventional chemical processes that utilise a distillation
process (non-catalytic) mainly consist of two separate unit
operations. These include a unit hosting chemical reactions
25   and another unit for separating the different components
from the resulting reaction mixture. Under such
circumstances, it is difficult to recycle the heat produced
by the chemical reaction, and cooling is often needed to
control the temperature in the reaction zone, thus resulting
30   in ineffective energy utilization in the process. In
addition, the productivity of a preferred compound is often

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limited by the conversion and selectivity in a chemical process due to equilibrium limitations. Since heat and mass transfer resistance are common problems in such a reaction unit, poor catalytic performance may occur together with a

5   shorter catalyst lifetime.

In order to avoid the chemical equilibrium limitation and make full use of reaction heat, the simple combination of a chemical reaction unit with the separation unit in a traditional distillation column has provided a successful

10   approach for a number of catalytic reaction processes. This combination was first utilized for homogeneous reaction systems. Because these systems involve both reaction and distillation, the name reactive distillation (RD) was coined for these processes. The traditional RD processes were

15   mainly based on homogeneous reaction systems; thus, RD is also referred to as homogeneous catalytic distillation. Although RD processes often result in both high reaction rates and high selectivity to certain desired products, several disadvantages still prevail. These include

20   separation of catalyst from the reaction products, recovery of catalyst, column fouling and corrosion. In addition, if the product purity with respect to the catalyst composition is strictly necessary, the products have to be intensively treated after reactive distillation to ensure a satisfactory

25   level of catalyst removal, which can increase operating costs.

For gas and/or liquid reactions occurring on the surface of solid catalysts (heterogeneous systems), reaction products can be easily separated from the catalyst system. If a

30   heterogeneous reaction can be managed within a distillation unit, the difficulty of separation encountered in homogeneous catalytic distillation can be overcome. However, another factor that must be addressed is to ensure that

sufficient catalyst is placed into the column without
significantly increasing the pressure drop. It was not
until 1980 that Smith (1980) patented a method of suspending
catalyst pellets inside a distillation column using
5   fibreglass containment bags, which are known as Texas
teabags. Use of these bags permits the use of heterogeneous
catalysts without giving rise to large increases in pressure
drop. In contrast to homogeneous catalytic distillation,
heterogeneous catalytic distillation is preferentially
10 termed catalytic distillation (CD).

In the CD process, the solid catalyst has to be packed in a
suitable manner inside the distillation column so as to
maximize contact between vapour and liquid phases, but to
minimize column flooding. Indeed, various methods have been
15 reported for supporting or containing catalysts [Crossland
et al., US Patent 5,431,890; Hearn, US Patent 5,266,546;
Shelden, US patent 5,417,938]. It should be noted that with
all these methods, the catalyst is enclosed inside a device
which can increase the mass transfer resistance of the
20 liquid and gas phases in the column.

Since a catalytic distillation process combines
heterogeneous reaction and separation in a single
distillation column, the following advantages can often be
obtained over conventional fixed bed reactors:

25 i)   The capital and production costs are reduced
because two operations are combined in a single unit.

ii)   The energy consumption can be minimized as the
heat of the reaction is used for the in-situ vaporization of
the reactants.

30 iii)   The conversion of the reactant can be enhanced
through internal recycling.

iv)   As the reaction products are continuously removed from the reaction site or the surface of catalyst as they are formed, the normal chemical equilibrium limitation does not apply, thus allowing a higher conversion to be achieved.

5 v)   The selectivity for a desired product can also be improved by continuously removing of the product away from the reaction site or the catalyst surface as the product is formed.

vi)   The heat generated by the reaction can be
10 efficiently carried away by the liquid and vapour, thus eliminating or avoiding the formation of hot spots on or in the vicinity of the catalytic site. This movement of the flushing liquid or vapour has a flushing effect in that it removes the higher molecular weight oligomerization products
15 down from the reaction zone, and thereby freeing the catalytic site for another reaction. The possible fouling and poisoning of the catalyst are greatly reduced.

vi)   The catalyst lifetime can also be improved because the catalyst bed is surrounded by hot or boiling liquid and
20 vapour that constantly exert a flushing on the catalyst site. Such a flushing effect remove products and by products that can undergo further reaction which can lead to possible fouling and poising of the catalyst.

Although there are many advantages for CD technology over
25 the conventional processes mentioned above, catalytic distillation is not suitable for use in all chemical reaction process. In order to achieve the benefits from a CD process, a chemical reaction system should preferably satisfy the following requirements:

30 i)   The reaction should take place in the liquid phase.

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ii)   The catalyst should be heterogeneous and stable thermally as well as chemically and physically to retain its structural integrity for maintenance of a long lifetime.

iii)   The reaction should be exothermic and in
5   situations where the reaction is equilibrium limited, the CD process presented the option to shift that equilibrium more to the right to achieve higher conversion and higher productivity much more efficiently.

One chemical reaction that satisfies these requirements is
10   the oligomerization of lower alkenes (alkene molecules having from 2 to 6 carbon atoms). Alkylation and oligomerization of lower alkenes was first disclosed by Huss and Kennedy (1990) and Smith et al. (1991). The oligomerization of lower alkenes is an important industrial
15   reaction and represents a route to the production of intermediates used for the production of motor fuels, plasticizers, pharmaceuticals, dyes, resins, detergents, lubricants and additives (O'Connor and Kojima, 1990). With respect to butene oligomerization, the less branched dimer
20   products, octenes, are particularly useful in the manufacture of plasticizers. If heavily branched, the mixture can be used as a gasoline blender.

Historically, the exploitation of all of the C_4 fractions obtained as by-product from hydrocarbon fluid catalytic
25   cracking and steam cracking to produce high value products (high octane value product) has been lacking. Butadiene, a component of the by-product is useful for rubber production and is extracted from the by-product, leaving the remaining C_4 fractions as a mixture referred to as Raffinate I. The
30   isobutene that is contained in Raffinate I was used as a source for production of methyl tert-butyl ether (MTBE). The remaining components of the C_4 fractions after the removal of

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isobutene, consisting mainly of linear C_4 hydrocarbon
(butenes), was mainly used as a gasoline blender, albeit a
poor one. In certain cases, this product was simply disposed
of by flaring. In Raffinate II, n-butene is present at an
5   average content from 70% to 80% and in some cases can be in
the ninety percentage ranges. Using this resource, smaller
oligomers, particularly C_8 and C_{12}, are being produced by
current catalytic oligomerization processes.

A variety of butene oligomerization processes have been
10 proposed (Keim et al., 1979; Mathys, 1984; Beltrame et al.,
1994) based on homogeneous and heterogeneous reactions.
These processes are exclusively focused on the catalyst
selection and process optimization so that a high
oligomerization rate with a high selectivity to desired
15 products, mainly short and less branched oligomers, can be
obtained.

The use of catalytic distillation to enhance the
oligomerization of alkenes was first disclosed in US Patent
No. 5,003,124 to Smith in 1991. This process utilized an
20 acidic ion exchange resin placed inside a fibre glass bag.

Further research has been carried out in the field of alkene
oligomerization, but in most cases, the oligomerization
catalyst is contained within a second structure such as a
cloth or mesh bag, and the reactants have to pass through
25 this structure to access the catalyst. Likewise, the
products have to pass through the structure to be removed
away from the catalyst. In one such example, Podrebarac
(1992) studied butene dimerization in a CD column using a
nickel exchanged zeolite catalyst, where the zeolite was
30 placed directly in fibreglass bags. The zeolite catalyst in
this case was quickly deactivated by the production of   •
undesirable long chain oligomers, which oligomers blocked

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the active sites on the catalyst. The system also displayed poor selectivity to octane due to the mass transfer resistance caused by the fibreglass bags.

Additional work has been carried out to find alternative
5   methods of placing the catalyst directly in the reactive zone of the distillation column, without resorting to the containment of the catalyst in secondary structures such as cloth or mesh bags.

US Patent 6,291,719 B1 to Gao et al. discloses dual-
10   functional catalyst structures having very specific shapes. These catalyst structures, which are formed from a resin catalyst, a metal oxide superacid catalyst or a molecular sieve catalyst, are shown to be suitable for etherification reactions, alkylation reactions, hydrogenation reactions and
15   for the decomposition of MTBE. US 6,291,719 B1 discloses catalyst structures which are limited to two very specific shapes, and the materials used also possess markedly low surface area values.

US Patent No. 5,244,929 to Gottlieb et al. also discloses
20   moulded organic catalyst bodies made of strongly acid or basic ion exchange resins.

SUMMARY OF THE INVENTION

In one aspect, the present invention provides a catalytic composite for use in a catalytic distillation apparatus, the
25   catalytic composite comprising:

        a) a support structure, made of an inorganic oxide, having a void fraction ranging from 0.30 to 0.95, a surface area of from 40 m^2/g to 500 m^2/g, and a crush strength of from 2.4 to 9.9 kg per structure unit, the
30   support structure having a shape selected from a ring, a

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hollow cylinder, a cross or multi partition ring or cylinder
with 2, 3, or 4 cell partitions, a saddle, a solid ring, a
solid cylinder, a sphere, and a honeycomb body; and

     b) from 0.01 to 10% by weight of a catalytically
5   active species, based on the weight of the catalyst, which
is deposited on the support structure.

In another aspect, the present invention provides a
catalytic composite for use as a hydrogenation catalyst in a
catalytic distillation apparatus, the catalytic composite
10 comprising:

     a) a support structure, made of an inorganic
oxide, having a void fraction ranging from 0.30 to 0.95 and
a crush strength of from 2.4 to 9.9 kg per structure unit,
the support structure having a shape selected from a ring, a
15 hollow cylinder, a cross or multi partition ring or cylinder
with 2, 3, or 4 cell partitions, a saddle, a solid ring, a
solid cylinder, a sphere, and a honeycomb body; and

     b) from 0.01 to 10% by weight of palladium,
platinum or rhodium, based on the weight of the catalytic
20 composite, which is deposited on the support structure.

In still another aspect, the present invention provides a
process for the selective oligomerization of a lower alkene
to a C_6–C_{18} alkene, which process comprises contacting the
lower alkene with a catalytic composite as described herein,
25 under catalytic distillation conditions.

In still another aspect, the present invention provides a
process for the hydrogenation of an alkene to an alkane,
which process comprises contacting the alkene with a
catalytic composite as described herein, and hydrogen, under
30 catalytic distillation conditions.

In still another aspect, the present invention provides a process for preparing high octane compounds, the process comprising:

    a) contacting a C_2 to C_6 alkene with a catalytic
5 composite as described herein, under catalytic distillation conditions, to obtain a C_6 to C_{18} alkene; and

    b) contacting the C_6 to C_{18} alkene from step a) with a catalytic composite as described herein which is suitable for hydrogenation, and hydrogen, under catalytic
10 distillation conditions, to obtain a C_6 to C_{18} alkane.

In still another aspect, the present invention provides a process for preparing high octane compounds, the process comprising:

    a) contacting isobutene with a catalytic composite
15 as described herein, under catalytic distillation conditions, to obtain trimethylpentene; and

    b) contacting trimethylpentene with a hydrogenation catalyst, and hydrogen, under batch reaction conditions or under hydrogenation reaction conditions to
20 obtain trimethylpentane.

In still another aspect, the present invention provides a process for the production of C_6-C_{18} alkenes, which process comprises contacting a mixture of C_2-C_6 alkenes with a catalytic composite as described herein, under catalytic
25 distillation conditions.

In still another aspect, the present invention provides a process for the selective oligomerization of a lower alkene to a C_6-C_{18} alkene, which process comprises contacting a mixture of C_2 to C_6 alkenes and C_1 to C_6 alkanes with a

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catalytic composite as described herein, under catalytic
distillation conditions.

In still another aspect, the present invention provides a
process for the hydrogenation of butadiene, the process
5   comprising contacting butadiene with a catalytic composite
composite as described herein which is suitable for
hydrogenation, and hydrogen, under catalytic distillation
conditions.

In still another aspect, the present invention provides a
10   process for the selective hydrogenation of methylacetylene
and propadiene in a C3 fraction to provide propylene, the
process comprising contacting the C3 fraction with a
catalytic composite composite as described herein which is
suitable for hydrogenation, and hydrogen, under catalytic
15   distillation conditions.

In still another aspect, the present invention provides a
process for the selective hydrogenation of allene and
propyne in a fluid catalytic cracking (FCC) stream, the
process comprising contacting the FCC stream with a
20   catalytic composite composite as described herein which is
suitable for hydrogenation, and hydrogen, under catalytic
distillation conditions.

In still another aspect, the present invention provides a
process for the selective hydrogenation of butadiene in a
25   raffinate I or a raffinate II stream to provide a butene,
the process comprising contacting the raffinate I or the
raffinate II stream with a catalytic composite composite as
described herein which is suitable for hydrogenation, and
hydrogen, under catalytic distillation conditions.

30   Specific embodiments of the present invention will be better
understood when consideration is given to the following

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description, including the examples and tables of data
presented therein.

DESCRIPTION OF THE EMBODIMENTS

Base Materials for the Support Structure

5   The catalyst support material (support structure) can be
selected, for example, from inorganic oxides. Examples of
suitable inorganic oxides include alumina, zirconia, silica,
titania and any chemical and physical combinations thereof,
such as silica/alumina. Mixtures of structurally designed
10 materials such as molecular sieves and zeolites with
selected inorganic oxides are also suitable combinations for
use as catalyst supports. Of these, alumina is preferred,
and γ-alumina is more preferred. The inorganic oxides,
including the structurally designed materials, are
15 commercially available as powdered materials which serve as
the base material for support structures.

Support Structures

The powdered base materials can be shaped, moulded or
otherwise formed into specific structures (herein referred
20 to as support structures) without compromising the integrity
of the materials (e.g. without altering the crystalline
state or the elemental composition and physical properties
of the materials). The support structure preferably takes a
specific shape or form, which shape or form is selected from
25 the various shapes such as rings or cylinders, cross or
multi partition rings or cylinders with 2 cell, 3 cell and 4
cell partitions, saddles (such as Intalox or Beryl saddles),
solid rings or cylinders, spheres, and honey comb bodies
(single or double).

The size of the support structure can vary, and different sizes can be used for columns having different dimensions. For example, the cylindrical support structures can be as large as 5 cm in diameter and as small as 6 mm. The

5   preferred ratio of length to diameter for these cylinders is 1:1, but this ratio can vary from 1:3 to 3:1.

In addition to the shape or form, the surface area of the catalytic support is important and is a factor taken into consideration when the catalytic support is selected for the

10   formation of the support structure. A catalyst support with a large surface area is highly desirable. The BET surface area of the support structure can be selected from within the range of from 40 to 600 m^2 /g depending on the process, the feed and the reaction. Preferably, the surface area

15   ranges from 60 to 450 m^2/g, and most preferably, from 80 to 350 m^2/g.

The support structure should be robust or strong. The crush strength of a support structure provides a relative measure of its strength and its ability to withstand attrition when

20   subjected to varying pressures and temperatures. The support structure preferably has a rush strength of from 2.4kg to 9.9kg per unit(i.e. per single structure) or per unit of the catalytic composite. The catalytic composite is obtained from the support structure after the deposition of

25   a catalytically active species, such as a metal compound or an acidic salt, on its surface.

The column void volume fraction is a feature that directly relates to the support structure when such structure is randomly packed in a reaction column (e.g. catalytic

30   distillation column). The shape or form of the support structure determines the column void volume fraction, which represents the fraction of space in the column not occupied

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by the solid portion of the support structure. The shape or form of support structure influences the void volume in two ways. Firstly, the space formed or enclosed within a hollow (volume enclosed wholly or partially) of the support

5 structure. Secondly, the space generated by the non-uniform orientation (relative angles assumed) of the support structure and interaction among the individual support structure when randomly loaded in the reactor column. The non-uniform orientation of the support structures does not

10 significantly hinder the overall flow of the liquid or vapour within the column, which is for practical purposes unidirectional, but it does provide a random distribution as gases or liquid flow through the packed structures. Such a flow pattern enhances gas or liquid contact with the support

15 structures, which permits a better conversion of vapour to liquid within the void spaces in the column and also lowers the mass transfer resistance through the reactive zone of the distillation column.

A void fraction of 1.0 represents a completely empty column,

20 while void fractions of 0.30 and 0.95 represent 30 and 95 percent of empty space in the column, respectively. The void fraction within the column which holds the catalytic composite or a combined mixture of catalytic composite plus inert support structures can range from 0.30 to 0.95.

25 Preferably, the void fraction is from 0.40 to 0.85, and more preferably the void fraction is from 0.55 to 0.70. For example, a catalytic composite in the form of a cylinder having a 6mm length and 6mm outer diameter gives a column void fraction of 0.50.

30 The haphazard flow pattern caused by the structures, the dilution of the amount of catalyst in the column, and the simultaneous fractionation and separation of the product collectively contribute to the selectivity of the reaction

carried out in a catalytic distillation column loaded with the catalytic composite described herein. These features can therefore be seen or defined as properties of the catalytic composite or properties a homogenous mixture of

5   the catalytic composite and the catalyst support structures when randomly packed in a column. Alternatively, these features can be termed as the random packing characteristics of the catalytic composite.

The surface features of the support structures affect the

10   amount of catalyst that can be loaded on such structures. Surfaces that are rendered smooth or non porous or glazed by the shaping process or otherwise, are undesirable for depositing a wide percentage variation of catalyst loadings. Only traces of catalyst (less than .01%) were found on

15   smooth or low porosity structures. This is most likely due to the fact that the sites that accommodate the catalyst are blocked by the shaping process. A certain level of surface unevenness or roughness aids in the loading of the catalyst. A range of possible pore sizes is desirable to permit a wide

20   range of catalyst loadings. BET adsorption studies of support structures and catalytic composites derived from alumina rings used herein showed both mesopores and micropores. Pore diameters range from 70 angstrom to less than 20 angstrom. The adsorption studies indicated that the

25   catalysts are mostly to be found in the mesopores of the structure.

The Catalytic Composite

The catalytic composite is comprised principally of two separate components, namely a support structure and an

30   active metal or metal ion species as catalyst. These are combined or synthesised by a procedure to produce a composite material without the loss of features and

properties comprising of both components to constitute or form the catalytic composite.

Various catalytically active species can be deposited on the support structures described above to give the catalytic

5   composite.   Examples of active species include metals and metal ions from Groups VI, VII and VIII. These metals or metal ions can be loaded from corresponding metal salts or metal complexes. Of these metals and metal ions, nickel ions loaded from nickel salts, which are especially

10   effective for the oligomerization of lower alkenes, are preferred as the active species for oligomerization.   More preferably, the nickel ions loaded from aqueous solutions of nickel sulphate, or aqueous solutions of nickel chloride and ammonium sulphate are used as the active catalytic species.

15   Metals used as the catalytic species for oligomerization are also preferably in the +1 or +2 oxidation state. As the oligomerization is acid catalysed, acid and acidic salts can be deposited on the support and used as catalyst. In addition, the oligomerization catalysts comprising nickel

20   ions can be further enhanced through exposure to solutions of sulphate salts such as ammonium sulphate, phosphate salts such as ammonium phosphate and acids such as sulphuric acid, phosphoric acid or toluenesulfuric acid. Such solutions are herein referred to as catalyst enhancers.

25   The catalytically active species are not necessarily metallic, as certain salts, such as ammonium sulphate, can be used. For example, ammonium sulphate is a suitable catalytically active species for the dimerization of isobutene in the presence of hydrogen.

30   Metal loaded from metal complexes of palladium, platinum, rhodium and nickel are effective for hydrogenation of alkenes, including hydrogenation of octenes and methyl

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substituted pentenes produced by the oligomerization of
butenes by the nickel catalyst described herein. Metal
salts can also be used as catalytic species in the
hydrogenation process if the metal ions derived from the
5   salts can be reduced to give metal species that are active.

The amount of catalyst species on the support structure is
dependent on the concentration of metal salt or the metal
complex in solution, and to a lesser extent on the length of
the exposure period of the support structure to the
10   solution. The amount of catalytic species can be from 0.01
to 10% by weight, for example of from 0.05 to 10% or from
0.1 to 8% by weight.

A catalytic composite for use as an oligomerization catalyst
can, for example, contain nickel in an amount of from 0.1 to
15   8% by weight, relative to the weight of the composite.
Preferably, the amount of nickel is from 0.2 to 6.0% by
weight, and more preferably, from 0.5% to 5% by weight.

A catalytic composite for use as a hydrogenation catalyst
can, for example, contain palladium in an amount of from
20   0.05 to 8% by weight, relative to the weight of the
composite. Preferably, the amount of palladium can be, for
example, from 0.1 to 8%, from 0.2 to 6%, from 0.2 to 5%,
from 0.5 to 5% or from 0.3 to 2% by weight.

Deposition of the metal ions on the support structure can be
25   effected by methods known in the art. Examples of such
methods include wet and dry impregnation methods,
vaporization methods, absorption techniques, ion-exchange
techniques, sol-gel techniques and vapour deposition
techniques. A description of such techniques is given in
30   examples 1a and 1b.

Catalytic Distillation Packing

The catalytic composite is effective as a material or a
media for the application as catalytic distillation packing
when used in a catalytic distillation column because of the
large surface area of the composite and the void space
5   obtained when the composite is randomly packed in the
column. The catalyst component of the catalytic composite
carries out the desired chemical reaction or reactions while
the surface area and the void volume is effective for
fractionation and separation of the reaction products. The
10   composite can therefore act as a catalyst as well as a
fractionation medium. Depending on the type of reaction,
the activity of the catalyst, or the level of separation
that is desirable, the catalytic composite can be mixed with
inert support structures (i.e. support structures that do
15   not contain a catalyst and are inert to reaction) and be
used in the catalytic distillation column as catalytic
distillation packing. The combination of catalytic
composite with support structures as catalytic distillation
packing material in a catalytic distillation column can
20   result in an increase in the selectivity of the catalytic
distillation process. This increase in selectivity is due
to: i) an increase in the void space in the distillation
column, and ii) better control on the rate of conversion
within the distillation column. For example, in the present
25   invention the composite catalyst made from Raschig rings of
6mm can be combined with Intalox saddles (inert support
structure) in a 1:1 ratio to form a mixture and used as the
catalytic distillation packing. Such a randomly packed
mixture in the column gives a void volume fraction of 0.55
30   which is intermediate between that of the rings (0.49) and
the saddles (0.62). The presence of such support structures
as inert packing materials in the reactive zone can also
lead to a better control of the rate of conversion within
the distillation column. For exothermic catalytic

reactions, there is the possibility that the temperature
will increase uncontrollably as the heat produced by the
reaction increases the rate of reaction in an exponential
manner.   This is commonly referred to in the industry as
5   "temperature runaway".   Temperature runaway is especially
detrimental to the selectivity of certain reactions, such as
oligomerization reactions, as higher temperatures result in
the formation of unwanted products, such as the formation of
polymers instead of oligomers such as dimers. Using support
10 structures as inert packing material within the reactive
zone can therefore be beneficial, as they can be used to
control or lower the overall rate of conversion in the
distillation column by finely dispersing the catalytic
composite within the reactive zone. The inert support
15 structures act as a dilution medium for the catalytic
composite and at the same time provide additional surface
for fractionation to occur.   The ratio of such inert packing
material to catalytic composite can vary for different
catalytic active species.   The ratio of inert packing
20 material to catalytic composite can range, for example, from
10:1 to 1:10.

The support structure to be used as inert packing material
can be selected from any known packing material that is
suitable for use in catalytic distillation.   This packing
25 material can have various shapes, such as Raschig rings,
Pall rings, penta rings, wagon wheels, honeycomb rings, berl
saddles, Intalox saddles, Super Intalox saddles, Hy-Pak
packing, Tellerette packing, Maspac packing, Cascade mini-
rings, and Nutter rings.   The size of the random-packing
30 material used is dependent on the size of the diameter of
the distillation column, and it is usually similar in size
to the catalytic composite.   The inert packing material can
be made out of materials similar to those used for the

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support structure, such as alumina, zirconia, silica, and titania, but it can also be formed out of less porous materials such as silicon carbide, metals, ceramic, and plastics.

5 *Reactants and Products*

In the description, the expression "lower alkenes" refers to alkene molecules that have 2 to 6 carbon atoms. Of primary interest are those alkenes that have 4 carbon atoms (1-butene, 2-butene, and isobutene).

10 The products of the selective oligomerization process of the present invention are principally the dimers and trimers of the C_2 to C_6 alkenes. These products include alkenes having from 6 to 18 carbon atoms, although the products of most interest are the dimers of the C_4 alkenes. These have the

15 general formula C_8H_{16}, and they are widely used in the petroleum industry as gasoline additives. The possible dimers of C_4 include trimethylpentenes, n-octenes, dimethylhexenes and methylheptenes, of which dimethylhexenes and trimethylpentenes are of greater interest, since the

20 more branched octenes have a higher octane number. In particular, hydrogenation of 2,4,4-trimethylpentene-1 and 2,4,4-trimethylpentene-2 can produce 2,2,4 trimethylpentane which has an octane number of 100. Surprisingly, the octene product obtained from the dimerization of 1-butene produced

25 through the catalytic distillation process of the invention is enriched in dimethyhexenes compared to the octene product obtained from the batch and flow reactors. As dimethylhexenes have a higher octane number than methylheptenes, dimerization of 1-butene in a catalytic

30 distillation column provides added benefit in the form of a higher value octane product from the dimerization of 1-butene.

Process Setup and Optimization

The process of the invention is termed "selective", as the
catalytic distillation process using the composite catalyst,

5   or the composite catalyst in admixture with inert support
structures, permit a reaction that is selective in
generating and removing octenes from the reaction stream.
In conventional oligomerization reactions, many products are
formed and the resulting mixture of products has to be

10 purified to isolate the desired product. The production of
the mixture also limits the overall selectivity of the
reaction. With catalytic distillation however, the process
variables can be selected so as to enhance the production of
predominately a single product or group of products. The

15 process variables can also be selected to control the
reaction and to prevent intermediate products that would
have normally continued to react under conventional reaction
conditions.

Many process variables can be changed when carrying out a CD

20 process, and most of the variables can be optimized for
specific reactions or products. Such variables include the
position of the feeding inlet, the position of the reactive
zone, the operating pressure, and the feed rate.

• Position of Feed Inlet

25 The position of the feed inlet is important as it determines
where in the reactor CD column the lower alkene feed stock
is introduced and where the reaction commences within the CD
column. For the dimerization of 1-butene, it is preferable
to have the inlet for the introduction of the 1-butene in

30 the CD located below the catalyst zone or the reactive zone
of the column in order to obtain higher selectivity and

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productivity as compared to when the inlet was located above the catalyst zone or reactive zone (see data in Table 8).

The reaction following introduction of the feed stock above or below the catalyst zone produces a different temperature
5   profile along the catalyst zone and this in-turn affects the conversion and selectivity. The situation is same for isobutene and shown in example 7.

The position of the reactive zone, and therefore of the catalytic composite, in the column can also be varied to
10   optimize the reaction. For the selective dimerization of butene, it is preferred to keep the reactive zone fairly high in the column, as the lower sections usually have a high liquid phase temperature. This high temperature can result in a faster reaction, which favors the formation of
15   large oligomers instead of dimers.

•The Effect of Operating Pressure

The operating pressure within the column can also be varied to optimize the CD process. Variation of pressure in the column will change the temperature, and the pressure is
20   therefore chosen such that the temperature in the reaction zone is suitable for the chemical reaction to occur and such that a liquid phase is maintained in the reaction zone. For the dimerization of butene, the operating pressure can be, for example, from 90 to 115 psi, with higher pressures
25   increasing the butene conversion. However, care must be taken as increasing the pressure beyond a certain level can compromise octene selectivity.

•The Effect of Feed Rate

The feed rate of the reactant can also be varied to optimize
30   the reaction. High feed rates lead to higher production

rates, but they can also have a negative impact on the
selectivity of a reaction. In the oligomerization of C_4, the
selectivity of the C_8 product decreases as the feed rate
increases because the reaction has a greater tendency to

5   proceed to products of higher molecular weight such as C_{12}.
In the present invention, the feedstock is preferably mixed
with an inert solvent before being fed into the reactor.
The presence of the inert solvent reduces the concentration
of the reactant in the column, thus permitting a higher

10   selectivity in the reaction. Suitable solvents that can be
used include C_4 to C_8 alkanes, higher alkanes, cycloalkanes
and alkyl substituted cycloalkanes. Preferably, isopentane
is used as the inert solvent. In addition, the inert
solvent uniformly dissipates the heat generated by the

15   reaction and it assists in the extraction and removal of any
higher oligomers or coke precursors that could deactivate
the catalyst. As long as the mass transfer resistance is
kept fairly low, which can be achieved by using the
catalytic composite of the invention, the separation of the

20   product produced by the distillation column provides good
selectivity, even under higher feed rates.

Multiple Catalysts or Reactive Zones

The catalytic distillation column can also be fitted with
more than one catalyst or more than one composite catalyst

25   within the same reactive zone, to carry out more than one
reaction simultaneously. Alternately, the column can be set
up to have two reactive zones, where each zone may contain a
different catalyst or a different catalytic composite, where
each zone will be subjected to a different temperature

30   profile within the column. These reactive zones filled with
different catalysts or different catalytic composites and
operating at different temperatures within a single column
can therefore carry out more than one reaction, and as a

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result the column is being made to carry out more than one
process. This can be used, for example, when dimerization
and hydrogenation is required e.g. dimerization of butene
and hydrogenation of the octene produced. In such a case,

5   one of the reactive zones may comprise a composite catalyst
such as that given in example 1a for oligomerization and the
other reactive zone can comprise a composite catalyst with a
hydrogenation catalyst species such as platinum or
palladium. Multiple catalysts and catalytic composites in

10   one or more reactive zones can be used for the concurrent or
consecutive dimerization of a mixture of different alkenes
such as those derived from steam cracking, thermal and
catalytic cracking of hydrocarbons. Examples of such
mixtures include raffinate streams from steam cracking of

15   naphtha and the light gases obtained from the fluid
catalytic cracking (FCC) processes. Raffinate streams
usually comprise isobutene, 1-butene, 2-butene, butadiene
and butanes. A further raffinate stream, termed Raffinate
II, comprises primarily n-butenes, butanes and trace amounts

20   of butadiene. FCC gases comprise a mixture of C3, C4 and C5
alkenes or alkanes, in some instances, they can also
comprise C4 or C5 dienes.

Multiple catalytic distillation columns can also be combined
to carry out parallel, concurrent or consecutive reaction

25   processes. This can be used, for example, for the concurrent
or consecutive dimerization of a mixture of two or more of
1-butene, 2-butene and isobutene. This process can be
carried out in 2 or more separate columns using the same of
different catalysts or catalytic composites at the same or

30   at different catalyst loadings. Isobutene is more reactive
and dimerizes at a much lower temperature than 1-butene,
which in turn is more reactive than 2-butene. The first
reactive zone can be located at a lower temperature zone of

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the column to dimerize the isobutene, and the overhead
products containing mostly the remaining 1-butene and 2-
butene can then be fed to the second or third column which
contains a catalyst or catalytic composite in a reactive

5   zone of sufficient temperature to carry out the dimerization
of 1-butene and 2-butene. The use of two or more columns
provides the flexibility to place the catalytic composites
at different height or sections of the distillation column
to provide reactive zones with different temperatures and to

10   avoid the further undesirable oligomerization reaction. A
combination of multiple columns can also be used to carry
out different reactions in a sequential manner such as the
dimerization of isobutene and the hydrogenation reactions
described above for the production of isooctane (for example

15   2,4,4- trimethylpentane)

Single or multiple catalytic distillation columns can also
be used in conjunction with guard beds. The guard beds are
useful to separate unwanted reactants from the reactant
streams before such streams are introduced to the CD column.

20   For example, such an operation with a guard bed is useful
for a feed stream consisting of butene and butadiene where
the dimerization of a butene is required. In such case,
butadiene needs to be removed from the feed stream before
introduction into the distillation column since it is known

25   that butadiene can poison dimerization catalysts. A guard
bed that removes the butadiene by selective adsorption, or
that selectively hydrogenates the butadiene to butene can
thus be used to pre-treat the feed stream before it is fed
into the CD column.

30

EXAMPLES

The following examples are offered by way of illustration
and not by way of limitation.

EXAMPLE 1a: Preparation of a catalytic composite from a
5   metal salt

A typical catalytic composite was prepared by the wet
impregnation of nickel sulphate onto a support structure
derived from γ-alumina rings having a length and a diameter
of 6mm. 13.5g of nickel sulphate hexahydrate was dissolved
10 in 70ml of deionized water. This solution was then
transferred to a container (beaker) containing 100g of the
support structure (γ-alumina rings). The container was gently
tumbled for about 3mins to achieve a uniform contact between
the solution and the rings. After an additional 30mins of
15 equilibration on the bench, the rings was allowed to dry in
air. This was followed by drying at 110° C for 12hrs. The
dried material was then calcined. The rings was placed in a
furnace preset at 110° C. The temperature was then ramped at
a rate of 5° C/min to a final temperature of 500° C.
20 Calcination was at 500° C for 12hrs after which time the
temperature was gradually lowered to room temperature. The
catalytic composite so obtained was removed and stored in
vials for use. The impregnation procedure was repeated to
obtain catalytic composites with an average nickel content
25 of 3% by weight.

EXAMPLE 1b. Preparation of a catalytic composite from a
metal complexes

The Pd catalytic composite was prepared by a wet-
impregnation technique, in which 0.34 g of Pd(acetate)$_2$ was
30 dissolved in a mixture of 50 mL of acetone and 50 mL of
water. This solution was added to 16 g of γ-alumina rings
25

(having a surface area of 204 m²/g) which were dried at 200
°C. The solution containing the γ-alumina rings was put into
a rotary evaporator and the solution was evaporated under
reduced pressure. The γ-alumina rings containing Pd were

5   dried in an oven at 90°C for 1 day, followed by calcination
in air at 350 °C for 3 hours and reduction in hydrogen at
350°C for 3 hours. The catalytic composite containing Pd
was protected from air. The weight of Pd in the catalytic
composite was 0.7 wt%.

10   EXAMPLE 2: Column Operational Set Up and Optimization

The catalytic distillation processes of the examples were
carried out on a CD column having a total height of 24 feet,
with an inner diameter of 1 inch and a total packing height
of 16 feet. The column is principally comprised of a

15   condenser of a total packing height that consists of three
segments. An upper non-reactive section, a reaction zone, a
lower non-reactive section with a reboiler. The non-
reactive sections is filled with catalyst support structure
as the inert packing material, such as the ¼″ Intalox

20   saddles, or any other known and suitable support structures
as mentioned before. The use of Intalox saddles in the non
reactive zone produced a void volume fraction of 0.62. The
reactive zone consists of the catalytic composite derived
from the alumina rings described in example 1 above, the

25   random packing of which produced a void volume fraction of
0.49. Alternatively, the total packing height may consist
of a mixture of the catalytic composite and the catalyst
support structure. For example the catalytic composite
derived from the alumina rings of example 1 and Intalox

30   saddles, a 1:1 mixture of which produced a void volume
fraction of such 0.55.

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The height of the total packing is dependent on the amount
of catalyst on the composite and the feed stock which
determines the nature of reaction. The catalytic
distillation column normally operates at total reflux. The

5   feed stock, for example 1-butene or isobutene, is mixed with
an inert solvent and fed into the column. The inert solvent
does not participate in the reaction but is used to
dissipate the heat generated by the reaction from the
reaction site. The solvent also facilitates the

10 extraction/dissolution and removal of any higher oligomers
or coke procurers that could potentially deactivate the
catalyst. Depending on the reactants, products and process
conditions for a particular operation, solvent can include
butanes, pentane, hexanes, higher alkanes and cycloalkanes

15 and alkyl-substituted cycloalkanes. For example, in the
dimerization of butenes, isopentane was found to be an
effective solvent. Alternatively, the packing material
within the column may be continuous, i.e. not segmented into
3 "zones". The packing material in such a case comprises

20 the catalytic composite of the invention alone throughout
the column, it comprises a substantially homogeneous mixture
of the catalytic composite with an inert packing material.

The following are additional examples of the effect of
various process parameters on the oligomerization of

25 butenes.

EXAMPLE 3. Effect of reboiler duty on the oligomerization of
butenes

The effect of reboiler duty on the CD process for the
dimerization and oligomerization of 1-butene was

30 investigated by varying reboiler duty from 200 W to 300 W
with a 1-butene feed rate of 48.17 g/h, isopentane feed rate
of 13.27 g/h, and 79.45 g of a catalytic composite

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containing 3.0 wt% Ni at a total pressure of 140 psig. The catalytic composite was mixed with an equal volume of ¼ in Intalox saddles. The results obtained are listed in Table 1.

Table 1: Reboiler duty effect on 1-butene oligomerization

	CD6-V	CD6-IV	CD6- I
Reaction conditions:			
Operating pressure, psig	140	140	140
Reaction temperature, °C	93-111	96-114	97-117
Reboiler duty, W	200	240	300
Amount of catalytic composite, g	79.45	79.45	79.45
Nickel concentration, wt%	3.0	3.0	3.0
Catalyst position, ft	12.5-14.5	12.5-14.5	12.5-14.5
Feed rate of 1-butene, g/h	48.17	48.17	48.17
Feed rate of isopentane, g/h	13.27	13.27	13.27
Feed position	Below	Below	Below
Results:			
Conversion, wt%	85.83	89.80	95.92
Selectivity, wt%	85.25	86.96	87.06
Productivity, g/g·h	0.52	0.54	0.58

5

•Selectivity represent the weight fraction of octenes out of total oligomers.

•Productivity represents the weight of oligomers produced by unit weight of catalytic composite per hour.

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It can be seen that when the reboiler duty increases, the
reaction zone temperature increases by a few degrees,
correspondingly the conversion increases from over 85% to
over 95%. Surprisingly although the conversion increases,

5   the selectivity to the octene dimer also increases. When
consecutive reactions such as the oligomerization of butenes
described in this invention was carried out in a
conventional reactor, normally the selectivity to dimers
decreases when the conversion increases. However, the

10   examples showed that when the oligomerization was carried
out in a catalytic distillation packing with this catalytic
composite with good mass transfer characteristics as
described in this invention, the selectivity to the octene
dimer unexpectedly also increased with the conversion.

15   The effect of reboiler duty on the oligomerization of
isobutene was also examined by increasing the reboiler duty
from 250 W to 380 W with an isobutene feed rate of 58.30
g/h, isopentane feed rate of 63.25 g/h, and 75 g catalytic
composite containing 1.5 wt% Ni mixed with an equal volume

20   of ¼ in Intalox saddles at a total pressure of 60 psig. The
results are listed in Table 2.

Table 2: Reboiler duty effect on isobutene oligomerization

	S1CD3	S1CD4	S1CD5	S1CD6
Reaction conditions:				
Reaction pressure, psig	60	60	60	60
Reaction temperature, °C	64-88	62-88	60-87	57-86
Reboiler duty, W	250	300	350	380
Amount of catalytic composite, g	75	75	75	75
Nickel concentration, wt%	1.5	1.5	1.5	1.5
Catalyst position, ft	10.7-12.7	10.7-12.7	10.7-12.7	10.7-12.7
Feed rate of isobutene, g/h	58.30	58.30	58.30	58.30
Feed rate of isopentane, g/h	63.25	63.25	63.25	63.25
Feed position	Below	Below	Below	Below
Results:				
Conversion, wt%	92.14	93.45	91.64	91.35
Selectivity, wt%	65.14	68.82	73.94	76.20
Productivity, g/g·h	0.72	0.73	0.71	0.71

•Selectivity represents the weight fraction of octenes out of total oligomers.

•Productivity represents the weight of oligomers produced by unit weight of catalyst per hour.

As the reboiler duty increases, the selectivity to octenes increased from over 65% to about 76 % although the

conversion remains essentially the same. This behaviour
showed that the feed rate is a little low for 75 g of the
catalytic composite since essentially all the isobutene is
converted. This example displayed that an increased

5 reboiler duty leads to an increase in reflux flow rate and a
better selectivity for the octene dimers.

For the oligomerization of 1-butene or isobutene, it is
demonstrated that as the reboiler duty increases, the
selectivity to octenes increases, which shows that the

10 catalytic composite is effective for both reaction and
separation. Since isobutene is more reactive than 1-butene,
a lower system pressure which results in lower temperatures
in the distillation column, and a lower Ni loading on the
catalytic packing are found to be more suitable for the

15 oligomerization of isobutene.

EXAMPLE 4. Effect of operating pressure. Oligomerization of
1-butene

The effect of operating pressure on the oligomerization of
20 1-butene was investigated by changing the operating pressure
from 90 psig to 140 psig, with a 1-butene feed rate of 48.17
g/h, isopentane feed rate of 13.27 g/h, and 142 g of
catalytic composite containing 3.0 wt% Ni and mixed with 1.2
times the volume of ¼" ceramic Intalox saddles. The results
25 obtained for 1-butene oligomerization are listed in Table 3.

Table 3: Operating pressure effect on 1-butene
oligomerization

	CD-7-I	CD-7-III	CD-7-IV
Reaction conditions:			
Operating pressure, psig	90	115	140
Reaction temperature, °C	83-104	94-115	106-122
Reboiler duty, W	300	300	300
Amount of catalytic composite, g	142	142	142
Nickel concentration, wt%	3	3	3
Catalyst position, ft	10.5-14.5	10.5-14.5	10.5-14.5
Feed rate of 1-butene, g/h	48.17	48.17	48.17
Feed rate of isopentane, g/h	13.27	13.27	13.27
Feed position	Below	Below	Below
Results:			
Conversion, wt%	90.91	95.32	95.61
Selectivity, wt%	88.38	87.91	86.66
Productivity, g/g·h	0.31	0.32	0.32

- Selectivity represents the weight fraction of octenes out
5 of total oligomers

- Productivity represents the weight of oligomers produced by
unit weight of catalytic composite per hour

On increasing the operating pressure in a catalytic
10 distillation column, the temperature in the reaction zone

increased correspondingly. This resulted in an increased
conversion of 1 -butene from over 90% to about 96%.
However, the selectivity to octenes decreased slightly.

5   EXAMPLE 5. Effect of feed rate. Oligomerization of 1-butene

The effect of feed rate on the oligomerization of 1-butene
was investigated at first by increasing 1-butene feed rate
from 35.31 g/h to 66.37 g/h with 79.45 g catalytic composite
containing 3.0 wt% Ni at 140 psig total pressure mixed with
10   an equal volume of ¼ in Intalox saddles (Table 4).

Table 4: Effect of feed rate for 1-butene oligomerization

	CD6- VIII	CD6-I	CD6-VII
Reaction conditions:			
Operating pressure, psig	140	140	140
Reaction temperature, °C	99-118	97-117	91-107
Reboiler duty, W	300	300	300
Amount of catalytic composite, g	79.45	79.45	79.45
Nickel concentration, wt%	3.0	3.0	3.0
Catalyst position, ft	12.5-14.5	12.5-14.5	12.5-14.5
Feed rate of 1-butene, g/h	35.31	48.17	66.37
Feed rate of isopentane, g/h	9.96	13.27	17.69
Feed position	Below	Below	Below
Results:			
Conversion, wt%	96.71	95.92	88.03
Selectivity, wt%	87.27	87.06	87.51
Productivity, g/g·h	0.43	0.58	0.74

• Selectivity represents the weight fraction of octenes out of total oligomers.

• Productivity represents the weight of oligomers produced by unit weight of catalytic composite per hour.

The effect was further investigated by increasing 1-butene feed rate from 48.17 g/h to 85.63 g/h with 142 g catalytic

composite containing 3.0 wt% Ni and 1.2 times the volume of ¼ in Intalox saddles at 140 psig (Table 5).

Table 5: Effect of feed rate for 1-butene oligomerization

	CD-7-IV	CD7-V	CD7-VI
Reaction conditions:			
Operating pressure, psig	140	140	140
Reaction temperature, °C	106–122	101–122	96–122
Reboiler duty, W	300	300	300
Amount of catalytic composite, g	142	142	142
Nickel concentration, wt%	3	3	3
Location of catalyst, ft	10.5–14.5	10.5–14.5	10.5–14.5
Feed rate of 1-butene, g/h	48.17	66.37	85.63
Feed rate of isopentane, g/h	13.27	17.69	23.23
Feed position	Below	Below	Below
Results:			
Conversion, wt%	95.61	95.40	93.39
Selectivity, wt%	86.66	86.53	87.76
Productivity, g/g·h	0.32	0.45	0.56

5   • Selectivity represents the weight fraction of octenes out of total oligomers

• Productivity represents the weight of oligomers produced by unit weight of catalytic composite per hour

Increasing the feed rate increased the productivity. At the lower feed rate, the productivity is lower, and hence it is advantageous to maximize the productivity per g of catalyst by varying the feed rate. The effect of increasing the
5   isobutene feed rate from 58.30 g/h to 77.38 g/h with 75 g catalytic composite containing 1.5 wt% Ni and an equal volume of ¼ in Intalox saddles at 60 psig on the isobutene oligomerization is shown in Table 6.

Table 6: Effect of feed rate for isobutene oligomerization

	S1CD4	S1CD7
Reaction conditions:		
Operating pressure, psig	60	60
Reaction temperature, °C	62-88	48-56
Reboiler duty, W	300	300
Amount of catalytic composite, g	75	75
Nickel concentration, wt%	1.5	1.5
Location of catalyst, ft	10.7-12.7	10.7-12.7
Feed rate of isobutene, g/h	58.30	77.38
Feed rate of isopentane, g/h	63.25	40.25
Feed position	Below	Below
Results:		
Isobutene conversion, wt%	93.45	90.71
Isooctene selectivity, wt%	68.82	77.94
Productivity, g/g·h	0.73	0.94

• Selectivity represents the weight fraction of octenes out
of total oligomers.

• Productivity represents the weight of oligomers produced by
unit weight of catalytic composite per hour

It can be seen that the productivity also increased as the
feed rate was increased indicating that the productivity
could be optimized by the changing the feed rate. There is
an optimum ratio of catalyst amount and feedrate for maximum
productivity in a CD process.

EXAMPLE 6. Catalyst stability. Oligomerization 1-butene

The catalyst stability for the oligomerization of 1-butene could be seen in the data shown in Table 7.

5   Table 7: Catalyst stability for 1-butene oligomerization

	CD6- I	CD6-III	CD6-VI	CD6-IX
Reaction conditions:				
Time interval, h	0–41	48–58	84–92	114–122
Operating pressure, psig	140	140	140	140
Reaction temperature, °C	97–117	96–115	95–114	95–114
Reboiler duty, W	300	300	300	300
Amount of catalytic composite, g	79.45	79.45	79.45	79.45
Nickel concentration, wt%	3.0	3.0	3.0	3.0
Catalyst position, ft	12.5–14.5	12.5–14.5	12.5–14.5	12.5–14.5
Feed rate of 1-butene, g/h	48.17	48.17	48.17	48.17
Feed rate of isopentane, g/h	13.27	13.27	13.27	13.27
Feed position	Below	Below	Below	Below
Results:				
Conversion, wt%	95.92	96.12	95.63	95.30
Selectivity, wt%	87.06	86.48	86.49	88.29
Productivity, g/g·h	0.58	0.58	0.58	0.58

• Selectivity represents the weight fraction of octenes out of total oligomers.

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- Productivity represents the weight of oligomers produced by unit weight of catalytic composite per hour.

5   Over a period of 122 hours, at a reboiler duty of 300 W, 1-butene feed rate of 48.17 g/h, isopentane feed rate of 13.27 g/h, and 79.45 g catalytic composite containing 3.0 wt% Ni and an equal volume of ¼ in Intalox saddles at 140 psig, the conversion, selectivity and productivity are essentially the same over the 122 h period. These data showed that the

10   catalytic composite is very stable in the CD process for butene oligomerization. After the reaction was terminated, the catalytic composite was removed from the column. It was observed the catalytic composite remains intact indicating the mechanical strength of the composite is suitable for use

15   in the CD column. Surface area measurement of the catalytic composite before and after the oligomerization were 183.7 m^2/g and 182 m^2/g respectively, indicating the stability and resistance of the catalytic composite to deactivation.

20   EXAMPLE 7. Effect of Feed position. Oligomerization of 1-butene and isobutene.

The position of feed inlet to the distillation column, i.e. whether the feed was above or below the catalyst zone, while all the other process conditions such as pressure, catalytic

25   composite, reboiler duty and feedrate are kept the same, could also result in a change in productivity and selectivity. Examples obtained for 1-butene and isobutene are shown in Tables 8 and 9. The results show that variation of feed inlet position will have an effect on productivity

30   and selectivity.

39

Table 8: Feed position effect on 1-butene oligomerization

	CD5-I	CD5-II
Reaction conditions:		
Operating pressure, psig	130	130
Reaction temperature, °C	118-125	114-119
Reboiler duty, W	300	300
Amount of catalytic composite, g	84.64	84.64
Nickel concentration, wt%	3.0	3.0
Catalyst position, ft	10.5-12.5	10.5-12.5
Feed rate of 1-butene, g/h	51.60	51.60
Feed rate of isopentane, g/h	14.26	14.26
Feed position	Below	Above
Results:		
Conversion, wt%	94.39	86.89
Selectivity, wt%	70.10	65.46
Productivity, g/g·h	0.58	0.53
C8 productivity, g/ g·h	0.41	0.35

• Selectivity represents the weight fraction of octenes out
of total oligomers.

5   • Productivity represents the weight of oligomers produced by
unit weight of catalytic composite per hour.

For the oligomerization of isobutene, however, it is more
advantageous to feed above the catalytic zone (Table 9).

Table 9: Feed position effect on isobutene oligomerization

	S1CD4	S1CD9
Reaction conditions:		
Reaction pressure, psig	60	60
Reaction temperature, °C	62-88	55-84
Reboiler duty, W	300	300
Amount of catalytic composite, g	75	75
Nickel concentration, wt%	1.5	1.5
Catalyst position, ft	10.7-12.7	10.7-12.7
Feed rate of isobutene, g/h	58.30	58.30
Feed rate of isopentane, g/h	63.25	63.25
Feed position	Below	Above
Results:		
Conversion, wt%	93.45	91.47
Selectivity, wt%	68.82	74.97
Productivity, g/g·h	0.73	0.71
C8 productivity, g/g·h	0.50	0.53

• Selectivity represents the weight fraction of octenes out
of total oligomers.

• Productivity represents the weight of oligomers produced by
unit weight of catalytic composite per hour.

EXAMPLE 8.   Comparison of CD and Batch Reactors.
Oligomerization of 1-butene and isobutene.

The advantages of a CD reactor for the dimerization of
isobutene can be seen in Table 10.

5   Table 10: A comparison of the catalytic composite
performance among the different types of reactors for 1-
butene oligomerization

	Batch reactor	Flow reactor	CD reactor
Reaction conditions:			
Reaction temperature, °C	110	110	101-122
1-butene flow rate (g/h) or its amount (g)	40	13.37	66.37
Catalyst, g	3.0	10	79.45
Catalytic composite type	Ni/γ alumina	Ni/γ alumina	Ni/ γ alumina
Ni concentration, wt%	3.0	3.0	3.0
Catalyst size, mm	15	2.0	15
Reaction time or residence time (min)	60	44.88	71.82
Results:			
Conversion, wt%	29.83	71.61	88.03
Selectivity, wt%	78.91	64.81	87.51
Productivity, g/g·h	3.98	1.15	0.74

● Residence time represents the weight of catalytic
10 composite/ mass flow rate of 1-butene.

- Selectivity represents the weight fraction of octenes out of total oligomers.

- Productivity represents the weight of oligomers produced by unit weight of catalytic composite per hour.

5

Under similar reaction conditions such as temperature and reaction time, the conversion and selectivity of the oligomerization reaction carried out in a CD column is much higher than a batch reactor or a flow reactor. This shows
10 that the catalytic composite containing Ni under CD conditions gives a high conversion and selectivity to the octene dimer compared to a batch or flow reactor system.

EXAMPLE 9. Other Catalytic Active Species for
15 Oligomerization of Lower Alkenes

Besides $NiSO_4$ as a catalytic component on a porous support such as γ alumina, other catalytic material such as $(NH_4)Fe(SO_4)_2$, $FeSO_4$ and $(NH_4)_2SO_4$ are also active for the dimerization and oligomerization of isobutene (Table 11).

Table 11: Effect of different metal sulfates for isobutene
oligomerization

Reaction conditions:					
Reaction temperature, °C	65	65	65	65	65
Amount of Isobutene, g	45	45	45	45	45
Amount of catalyst, g	3	3	3	3	3
Catalytic phase	$(NH_4)_2Fe(SO_4)_2$	$FeSO_4$	$(NH_4)_2SO_4$	$NiSO_4$	$NiSO_4$
Support	$\gamma-Al_2O_3$	$\gamma-Al_2O_3$	$\gamma-Al_2O_3$	$\gamma-Al_2O_3$	$\gamma-Al_2O_3$
Ni concentration, wt%	0	0	0	1.5	3.0
$SO_4{}^{2-}$ concentration, wt%	10.3	5.2	4.9	2.5	4.9
Reaction time, min	75	60	60	60	60
Results:					
Conversion, wt%	3.7	50.6	33.9	14.20	53.1
Selectivity, wt%	61.6	17.3	46.3	38.0	25.0

• Selectivity represents the weight fraction of octenes out
5   of total oligomers.

EXAMPLE 10. Effect of Ni salts on the Oligomerization of 1-
butene

Table 12 shows the activity of different Ni compounds on a
porous support structure, based on γ alumina, for the
oligomerization of 1-butene. Ni sulphate is more active than
Ni chloride. Addition of NH_4Cl to $NiCl_2$ increased the
5   activity of $NiCl_2$. The surface area of the fresh and used
catalyst are not very different indicating that the
catalytic composites are quite stable. Table 13 shows that
for the 1-butene oligomerization, the porous γ alumina is
much more stable than the NaY zeolite or BaNaY zeolite used
10   to support the $NiSO_4$ or $NiCl_2$ as can be seen from the
reduction of the surface area of the used catalyst.

Table 12: A comparison of catalytic composite performance
prepared by different catalytic phases supported on the
porous γ alumina in the batch reactor

Catalyst	Support	Nickel loading (wt%)	Reaction conditions	Conversion (wt%)	Selectivity (wt%)	Surface area m²/g
$NiCl_2$	γAl_2O_3	5.53	110°C, 600psi, 2hrs	12.53	93.28	Fresh= 183.2 Used= 188.5
$NiCl_2$+NH₄Cl	γAl_2O_3	5.53	110°C, 600psi, 2hrs	28.85	87.89	Fresh= 185.7 Used= 190.1
$NiSO_4$	γAl_2O_3	4.04	110°C, 600psi, 2hrs	36.71	72.15	Fresh= 186.5 Used= 187.0
$NiSO_4$	γAl_2O_3	4.04	60°C, 600psi, 2hrs	19.15	77.35	Fresh= 186.5 Used= 188.3
NiMo	γAl_2O_3	>10	110°C, 600psi, 2hrs	19.85	38.11	Fresh= 148.1 Used= 144.1

• Selectivity represents the weight fraction of octenes out
5 of total oligomers

Table 13: A comparison of catalyst performance prepared
using different supports in a batch reactor

Catalytic Phase	Support	Nickel loading (wt%)	Reaction conditions	Conversion (wt%)	Select-ivity (wt%)	Surface area m^2/g
$NiCl_2$	γAl_2O_3	5.53	110°C, 600psi, 2hrs	12.53	93.28	Fresh= 183.2 Used= 188.5
$NiCl_2$	NaY	4.85	110°C, 600psi, 2hrs	52.15	69.51	Fresh= 622.9 Used= 182.4
$NiCl_2$	BaNaY	0.87	110°C, 600psi, 2hrs	39.18	81.58	Fresh= 581.5 Used= 363.2
$NiSO_4$	Al_2O_3	4.04	110°C, 600psi, 2hrs	36.71	72.15	Fresh= 186.5 Used= 187.0
$NiSO_4$	NaY	5.20	110°C, 600psi, 2hrs	41.82	73.26	Fresh= 635.8 Used= 211.9

• Selectivity represents the weight fraction of octenes out
of total oligomers.

EXAMPLE 11. One step production of isooctane from isobutene
oligomerization and hydrogenation in a CD column

This example shows that high selectivity for the one step
production of isooctane from isobutene can be achieved using
5   a process where two separate catalytic distillation   zones
are used in the same distillation column, the upper
catalyst zone containing a dimerization/oligomerization
catalyst and a lower catalyst zone containing a
hydrogenation catalytic composite. In the dimerization
10   zone, a Ni catalytic composite was mixed with an
approximately equal volume of intalox saddles. The
isobutene can be fed anywhere above or immediately below the
dimerization zone. The hydrogen should be fed below the
hydrogenation zone. In the dimerization zone, the catalytic
15   composite contained 1 wt% nickel. In the hydrogenation
zone, the catalytic composite contained 0.7 wt % Pd. Table
14 shows the results of the one step reaction. When no
hydrogen was fed into the column (see Run number 2-3), the
oligomers consisted of 84.9 wt% octenes, 13.5 wt% dodecenes
20   and 1.6 wt% hexadecenes, and the selectivity to octenes was
84.9 wt%. The octenes consisted of 77.8 wt% 2,4,4
trimethylpentene-1 and 22.2 wt% of 2,4,4 trimethylpentene-2.
When hydrogen was introduced into the catalytic distillation
column below the reaction zone containing the Pd catalytic
25   composite (Run number 2-2), over 98% hydrogenation of the
octenes to 2,2,4- trimethylpentane (octane rating of 100)
was achieved. Some hydrogenation of dodecenes and
hexadecenes also occurred. The presence of hydrogen did not
reduce the productivity for the dimerization of isobutene to
30   octenes and a slight increase in oligomerization was
observed in the given experiment. The hydrogen flow rate
should be controlled such that the amount of hydrogen fed is
sufficient to hydrogenate the oligomers. Lowering of the

48

reboiler duty from 350 W to 300 W did not significantly affect the productivity of octenes or the production of 2,2,4 trimethylpentane (Comparing Run number 2-5 and Run number 2-2). Comparison of Run number 2-5 and Run number 2-

5   8 in Table 14 shows that increasing the isobutene feed rate increased the oligomerization activity and also the productivity of 2,2,4 trimethylpentane.

Since the pressure in the column controls the temperature in a catalytic distillation column, the pressure in the column

10 should be such that the temperature profile in the CD column is suitable for producing the oligomers at the top section of the CD column and the hydrogenation occurs at the bottom section of the CD column. An example of the effect of pressure on the process is shown in Table 15. It can be seen

15 that on increasing the pressure, the temperatures in the oligomerization zone and the hydrogenation zone increased, the oligomerization activity and the productivity of 2,2,4-trimethylpentane increased but the selectivity to octenes decreased.

20 The activities of the catalytic composites for dimerization/oligomerization and hydrogenation were stable over 20 days on stream.

Table 14: Effect of process parameters on production of 2,2,4 trimethylpentane from the oligomerization of isobutene and hydrogenation

Run number	2-3	2-5	2-2	2-8
Reaction conditions:	----	H$_2$	H$_2$	H$_2$
Temperature at Ni catalytic composite zone	75 °C	75 °C	75 °C	75 °C
Temperature at Pd catalytic composite zone	121 °C	121 °C	121 °C	121 °C
Reboiler duty, W	350	300	350	300
Amount of Ni catalytic composite, g	81.5	81.5	81.5	81.5
Amount of Pd catalytic composite, g	224.6	224.6	224.6	224.6
Ni catalytic composite position from reboiler, distance in feet	11.5-13.5	11.5-13.5	11.5-13.5	11.5-13.5
Pd catalytic composite position from reboiler,distance in feet	0.3-4.3	0.3-4.3	0.3-4.3	0.3-4.3
Feed rate of isobutene, g/h	49.95	49.95	49.95	62.85
Feed rate of isopentane, g/h	69.74	69.74	69.74	44.64
H$_2$ feed rate(L/hr @ STP)	----	8.77	8.77	13.21
Results:				
Oligomerization activity, g/g·h	0.51	0.51	0.54	0.85
Selectivity to octenes , wt%	84.9	86.37	87.32	84.37
Productivity of 2,2,4-trimethylpentane, g/g·h	-----	0.16	0.17	0.25

• Selectivity represents the weight fraction of octenes out
5   of total oligomers.

• Oligomerization activity represents the weight of octenes, dodecenes and hexadecenes produced by unit weight of catalyst per hour.

Table 15: Effect of pressure on production of isooctane from the oligomerization of isobutene and hydrogenation

Run number	4-17	4-15	4-18
Reaction conditions:	H_2	H_2	H_2
Temperature at Ni catalytic composite zone	76 °C	78 °C	85 °C
Temperature at Pd catalytic composite zone	124°C	125°C	130 °C
Pressure, psig	100	125	150
Amount of Ni catalytic composite, g	81.5	81.5	81.5
Amount of Pd catalytic composite, g	224.6	224.6	224.6
Ni catalytic composite position from reboiler, distance in feet	11.5-13.5	11.5-13.5	11.5-13.5
Pd catalytic composite position from reboiler, distance in feet	0.3-4.3	0.3-4.3	0.3-4.3
Feed rate of isobutene, g/h	68.37	68.37	79.83
Feed rate of isopentane, g/h	78.46	78.46	66.83
H_2 feed rate(L/hr @ STP)	8.77	8.77	15.01
Results:			
Oligomerization activity, g/g·h	0.79	0.83	0.92
Selectivity to octenes , wt%	85.24	83.07	58.73
Productivity of 2,2,4-trimethylpentane, g/g·h	0.20	0.20	0.28

• Selectivity represents the weight fraction of octenes out of total oligomers.

• Oligomerization activity represents the weight of octenes,
dodecenes and hexadecenes produced by unit weight of
catalyst per hour.

5   EXAMPLE 12. Hydrogenation of butadiene

3.7 g of Pd acetylacetonate was dissolved in 100 g of
dichloromethane, and the solution obtained was added to 50 g
of α-alumina rings of diameter and length of 8 mm (surface
area 0.22 m^2/g) which were dried at 200°C. The solution
10   containing the α-alumina rings was shaken at room
temperature for 24 hours. The α-alumina rings containing Pd
were taken out from the solution and dried in oven at 90°C
for 24 hours. Calcination was carried out at 350°C for 3
hours, followed by reduction with hydrogen at 350°C for 3
15   hours. The catalytic composite was protected from air. The
weight of Pd in the catalytic composite was 0.31 wt%.

Hydrogenation of butadiene in a mixture of butadiene and
isobutene was carried out in a batch autoclave using the
above catalytic composite. Selective hydrogenation of
20   butadiene to 1-butene and 2-butenes and n-butane was
obtained between temperatures of 50-90°C and pressures of
160-300 psig in a batch autoclave, for a mixture containing
5.4 wt% butadiene in isobutene. The catalytic composite
weight was between 1.63 to 2.45 g with Pd loading of
25   0.31wt%. In about 2-4 hours, 100 % hydrogenation of
butadiene was obtained.

All publications, patents and patent applications cited in
this specification are herein incorporated by reference as
if each individual publication, patent or patent application
were specifically and individually indicated to be
5   incorporated by reference. The citation of any publication
is for its disclosure prior to the filing date and should
not be construed as an admission that the present invention
is not entitled to antedate such publication by virtue of
prior invention.

10   Although the foregoing invention has been
described in some detail by way of illustration and example
for purposes of clarity of understanding, it is readily
apparent to those of ordinary skill in the art in light of
the teachings of this invention that certain changes and
15   modifications may be made thereto without departing from the
spirit or scope of the appended claims.

            It must be noted that as used in this
specification and the appended claims, the singular forms
"a", "an", and "the" include plural reference unless the
20   context clearly dictates otherwise. Unless defined otherwise
all technical and scientific terms used herein have the same
meaning as commonly understood to one of ordinary skill in
the art to which this invention belongs.